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CARBON DIOXIDE IN CAVE ATMOSPHERES. NEW RESULTS IN BELGIUM AND COMPARISON WITH SOME OTHER COUNTRIES

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ABSTRACT

More than 600 measurements of the carbon dioxide content of cave air in Belgium lead up to the conclusion that the main factors of its distribution are: (1) a flow originating from the biomass and diffusing in the soil and the voids of bedrock; (2) a trend, discernible in very still air only, to go down by density; (3) in some caves, draughts caused, for instance, by a swift underground stream.

Results in Belgium are compared with published and unpublished data from other countries, showing that CO_2 is often less abundant in cold climate caves and in caves of semi-arid regions (influence of the biomass).

Special attention is paid to human contamination during analyses: the influence of people passing through the cave nearby the operator, but also the influence of the operator himself are discussed, and the use of special precautions (including a CO_2-absorbing mask) in defined critical situations is stressed.

KEY WORDS Carbon dioxide Caves Human contamination Seasonal variations

INTRODUCTION

Carbon dioxide is of paramount importance in limestone solution. Although the action of other acids is neither ignored nor underestimated here, it is obvious, at least in temperate and cold regions, that carbonic gas is in most cases the prime mover and the main agent of carbonate dissolution.

Carbon dioxide in water comes either directly from the air or from the metabolism of the biomass—and in this case also, often through a gaseous phase—hence the primordial interest of knowing the CO_2 concentrations and movements in the limestone environments, particularly in cave air, in soil air and in the lowermost atmosphere.

More than 600 measurements of carbon dioxide have been carried out in Belgium, all of them carefully located in space, time and weather conditions. We try here to summarize in a few pages the main results of these analyses and to compare them with some other studies of carbonic gas all over the world.

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METHODS AND TECHNIQUES

Methods of measurement

All our recent measurements are done with a gas pump detector (Bendix–Gastec). The Gastec detector tubes (2 LL or 2 L) give a direct reading of the CO_2 concentration in the air (ppm/vol).* Before, an electrolytic field device had been used (Koepf, 1952; Hilger, 1963; Delecour, 1965; Ek *et al.*, 1968; Delecour *et al.*, 1968). This system, based on the electrolysis of a NaCl solution which had absorbed CO_2, is more precise ($\pm$ 0·1 mg CO_2/l i.e. $\sim$ 60 ppm: Ek, 1981) but heavier and slower. Thus, for field investigation, the Gastec pump system is more useful: it is very light and only 2 or 3 minutes are needed for one measurement. The minimal precision, guaranteed by the manufacturer, is $\pm$ 25 per cent but it seems that the effective precision is better and the reproducibility of measurements is $\pm$ 10 per cent (Ek *et al.*, 1981). When we express the results in ppm/vol, we refer to the Gastec detector measurements. For older measurements done with the electrolytic method, we keep the expression of the results in mg CO_2/l. The equivalence depending among other things on temperature is about 0·18 mg/l = 100 ppm/vol in TPN conditions.

Precaution during the measurements

With respect to the human breathing out CO_2 (about $40 \cdot 10^3$ ppm: Miotke 1974), it is very important to avoid human exhalation during the measurements. A carbon dioxide absorber system has been systematically used when measurements have been carried out in fissures, joints, and confined atmosphere. This system, described in Figure 1, is composed of a plexiglas surrounding wall in the form of a Y branch, with two valves of large diameter ($\sim$ 2·5 cm). The inlet valve opens to the cave air, and the air breathed in and out is ejected through the outlet valve into a stainless steel reservoir filled with soda lime. The exhaled CO_2 is then absorbed by this soda lime. A rubber mouth piece—coming from a snorkel—is fixed to the plexiglas surrounding wall and a nose clip obliges the operator to breathe by the mouth. The rubber mouth piece combined with the nose clip is more comfortable than the 'total' nose and mouth mask we used before. The necessity of using this CO_2 absorber system is evident and will be demonstrated later. In the same way, we do not use acetylene (carbide lamp), but only electric light during analyses.

RESULTS AND DISCUSSION FOR BELGIAN CAVES

Fissures versus larger passages

Cave air generally contains more carbon dioxide than the open atmosphere. Under temperate conditions, the CO_2 pressure in the caves is generally two to twenty times higher than in open air, sometimes more. In the caves, the first differentiation to appear to the air-analyst is grossly related to the width of the cavity: the fissures generally display a higher CO_2 content than larger passages, namely galleries and chambers. In the Trou Joney, at Comblain, a very shallow cave, values of 7·8 and 10·6 mg CO_2/l air (approximately 4300 and 5900 ppm) measured in fissures in July 1966 were 3 or 4 times higher than the values displayed by the passageways (Ek *et al.*, 1968). Similar observations were carried out in Poland (Ek *et al.*, 1969). In Brialmont Cave and in Ste-Anne Cave, both at Tilff, fissures have a higher CO_2 content than the respective passages of these caves (see Figure 3). In Rochefort Cave, the pCO_2 is diminishing from the fissures to the bulk of the atmosphere of a large chamber, The Hell, both in May and September (Figure 2). The strong gradient of pCO_2 at the outlet of the fissure seems to indicate that the carbon dioxide diffuses from the crack into the chamber (Delecour *et al.*, 1968; Ek, 1969).

Some fissures do not display a high pCO_2. But, although not universal, the distinction between fissures and

*To convert the CO_2 concentration (in ppm by volume) into partial pressure (pCO_2 in atmosphere), the following expression can be used:

$$pCO_2 \text{ (in atm.)} = \frac{\text{ppm } CO_2 \times (P\text{atmos.} - Pw)}{760 \cdot 10^6}$$

where: *P*atmos. = barometric pressure (in mm Hg)
Pw = water vapor pressure (in mm Hg)
(9 mm Hg at 10°C)

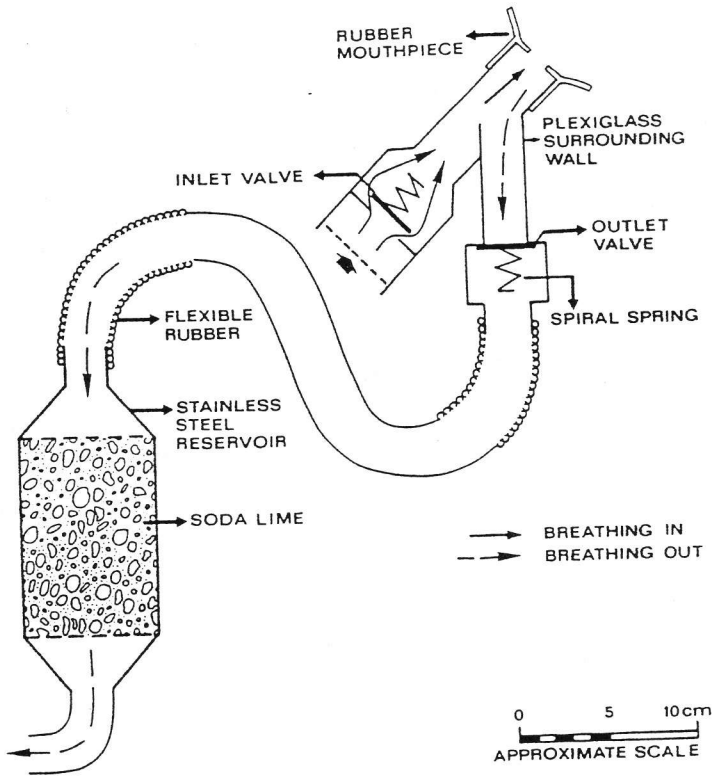

Figure 1. CO_2-absorbing device used in confined sites. The air breathed out by the operator passes through soda lime before being returned to the cave atmosphere

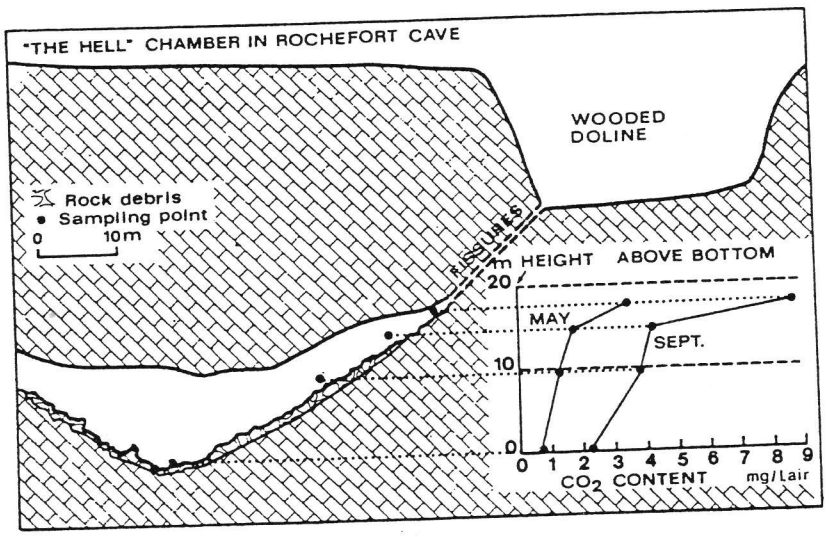

Figure 2. CO_2 titrations in the air of 'The Hell', a large chamber in Rochefort Cave. Cross-section showing sampling locations and CO_2 measurements of May 12, 1966 and September 13, 1969 (modified from Delecour *et al.*, 1968)

larger passages is very general, particularly in shallow or not too deep caves. In Belgium, most accessible fissures are in the upper part of the galleries and passages, and thus, as for fluids, there is likely to be a possible connection between the soil and the cave. This probably explains, for instance, that the gradient of CO_2

between the cracks and the main passages is steeper in Brialmont Cave (a very shallow cave) than in Ste-Anne, which is deeper lying.

Flow of carbon dioxide from the surface soil

As shown in Figure 2, the maximum pCO_2 is observed, in the cave considered, in a fissure connected with the ground below a wooded doline. This fact, and the downward gradient shown on this figure from the fissure, were often observed.

The observations indicate that CO_2 is coming through the cracks from the soil, from which biogenic CO_2 originates. This is corroborated by water analyses (Ek, 1969): the titrations of 32 underground seepage waters allowed the calculation of pCO_2 of an atmosphere in equilibrium with these waters: this pressure is 10 to 30 times higher than normal pCO_2 in open air. This is, in Belgium, generally not true of underground rivers, but it is of underground seepage waters, dripping from the ceiling, and thus coming from the soil.

A similar conclusion is reached by Delhez (1972) about the importance of biogenic processes on CO_2 abundance in caves. Yet in 1937, Adams and Swinnerton have shown that the CO_2 content in the soil is 25 to 90 times the amount of CO_2 normally found in the atmosphere.

Since then, a great number of CO_2 measurements have been done in the soil atmosphere, in varied edaphic environments. A lot of parameters (soil type, temperature, water content, level of biologic activity, etc) are involved in the CO_2 production in soils. More references on that matter can be found for example in: Atkinson (1977); Bakalowicz (1979); Bögli (1969, 1976); Dever *et al.* (1983); Dumont *et al.* (1983); Galimov (1966); Haas *et al.* (1983); Jakucs (1977); Miotke (1974); Nicod (1975); Paterson (1979); Rossi (1974, 1976, 1979); Russel and Russel (1950).

Seasonal evolution

The biogenic origin of most CO_2 induces a seasonal variation of its pressure. This was shown by Ek (1979) but was already suggested in Ek *et al.* (1968). The first clear and statistically significant confirmation of this fact was given by Gewelt and Ek (1985).

Figure 3 shows the differences between the pCO_2 figures of January and September obtained in two fissures, in a wet passage. January and September correspond respectively to the minimum and maximum values in most of the points shown in Figure 3. In these places, the CO_2 pressures observed in January are always less than one half of the September values.

Some 237 measurements were carried out in Ste-Anne Cave and Brialmont Cave in 1982 and 1983. Most of the results are summarized in Figures 4 and 5.

The seasonal evolution of the passageways is illustrated in Figure 4, which shows that in Brialmont Cave, lying a few metres beneath the soil surface, the CO_2 content of the air begins to increase in June and displays a maximum extending through the whole summer, whereas in Ste-Anne Cave, lying some eighty to one hundred metres below the surface of the plateau, the increase in CO_2 pressure is slow and leads in the main passages to a maximum at the end of September.

In the fissures, the fact that the flow of CO_2 is coming from the soil is obvious if one considers that the maximum pressure of CO_2 is earlier in Brialmont Cave than beneath in Ste-Anne Cave, but moreover the maximum is displayed earlier in the fissures of the upper level of Brialmont Cave, F1 and F2, than in the cracks F3 and F4 of the lower level of the same cave (see Figure 5).

The diffusion of CO_2 is schematically illustrated by Figure 6.

Vertical differentiation

In a single room or gallery the pCO_2 is frequently higher near the roof than near the ground. In this case, there is no static density equilibrium (CO_2 is denser than air) and the gradient is an inverse density gradient. This kind of vertical distribution as shown by Ek *et al.* (1968, 1969) may be related either with temperature, with air blow, or with humidity. The flow coming from the soil is perhaps warmer and above all richer in CO_2 which explains the high pCO_2 observed near the ceiling. This phenomenon of soil CO_2 coming from the fractured upper zone is clearly shown in Figure 2.

However, it is also frequent to observe a normal density gradient: CO_2 contents are higher near the bottom.

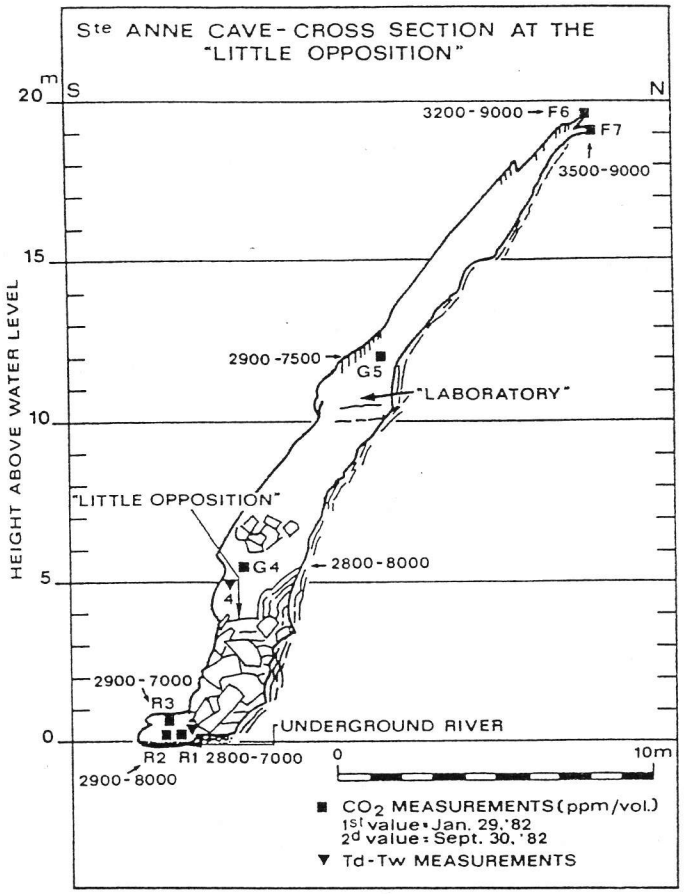

Figure 3. CO_2 titrations in Ste-Anne Cave. Cross-section of the main passage, 340 m east of the entrance, showing sampling locations and observed values in January and September. Squares refer to CO_2 measurements, triangles to temperature and moisture measurements. The cross-section is somewhat schematized, all points being not really in a vertical plane (after Gewelt and Ek, 1985)

For example in the Comblain-au-Pont cave (Figure 7), the pCO_2 increases from the entrance to the bottom. Nearby the entrance of the cave, the CO_2 content corresponds to the normal open air value (330 ppm), afterwards the pCO_2 increases to the bottom. An inversion was found in the little chamber situated 3·5 m over the bottom: the higher CO_2 content in this zone may be due to the diffusion or also to the confined morphology of the little chamber (Delecour *et al.*, 1968; Ek *et al.*, 1968).

The general downwards increasing CO_2 gradient can be due to an accumulation by gravity. This phenomenon can also be reinforced by a thermal inversion which catches the air near the bottom. Referring to the Figure 8 where the temperature variations (in °C) and relative humidity (percentage) are shown during one year in Ste-Anne and Brialmont caves, it can be seen that there is a thermal inversion in the main passage of Brialmont cave the whole year long. The cold air is always caught near the bottom of the gallery (G6) and the warmer air is located near the roof (G7). This thermal inversion is more important during the summer (difference of 2·5°C) and is accompanied by a CO_2 stratification which can be seen in Figure 4 (G6–G7) and Figure 5 (F1–F2, F3–F4) (Gewelt and Ek, 1985). The thermal inversion blocks the CO_2 and the colder air in the lower passage. A measurement done at mid-height (September 30, 1982), between G6 and G7 shows that the richer CO_2 layer is not only located near the bottom but also in the half of the height of the gallery. Thus the downwards CO_2 increasing gradient is related with a gravity stratification, accentuated by a thermic inversion. This may be a normal situation in caves where air circulation (and ventilation) are reduced and where stratification is possible. Vertical caves are probably a better trap for CO_2.

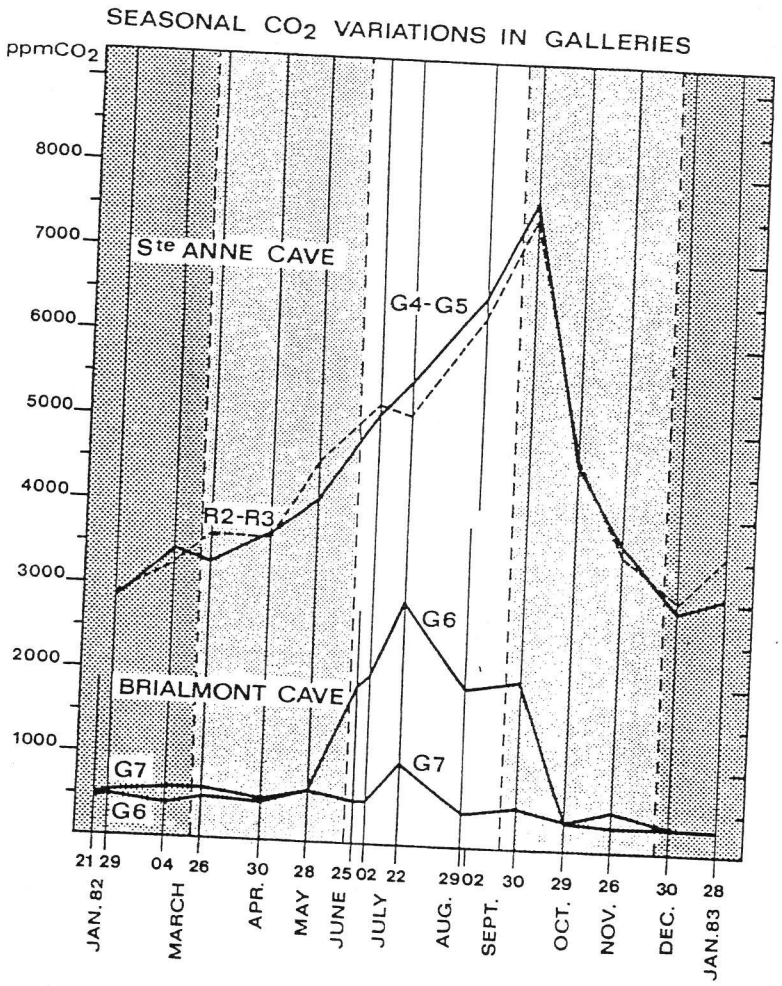

Figure 4. Seasonal evolution of the CO_2 content of the main passages of Ste-Anne and Brialmont Caves. R: wet passage: the underground river; G: dry passageway (modified from Gewelt and Ek, 1985)

In Figure 8 it can also be seen that the relative humidity in Ste-Anne cave is very high and constant (98 to 100 per cent). This short range may be correlated with the confined zone where measurements were done and with the presence of an underground river. Dripping water contributes also to the saturation of the cave atmosphere. In Brialmont cave, the relative humidity is always high but more variable (from 91 to 100 per cent), as a consequence of the two opposite entrances and better ventilation.

Horizontal gradient

An horizontal gradient of CO_2 is frequently observed in horizontal caves. This was shown for the first time by Ek *et al.* (1969) in a Polish cave, during the winter. The CO_2 gas in the cave atmosphere becomes more and more abundant towards the end of the cave, because the distal zones are more confined.

The same phenomenon, but above the Rubicon river in the Remouchamps cave, is shown in Figure 9. CO_2 contents of air 20 cm above water level decreases from the sump to the exurgence. The water is in equilibrium with high CO_2 values and when the river emerges from the sump and enters in the accessible passage of the cave, CO_2 comes out the water to the air (the diffusion rate is very high). The CO_2 excess of the water becomes lower downstream and the cave ventilation is improved, which leads to lower pCO_2 in the air above water level (Delecour *et al.*, 1968; Ek *et al.*, 1968).

An example combining the two factors (horizontal gradient and CO_2 supply by underground river to cave

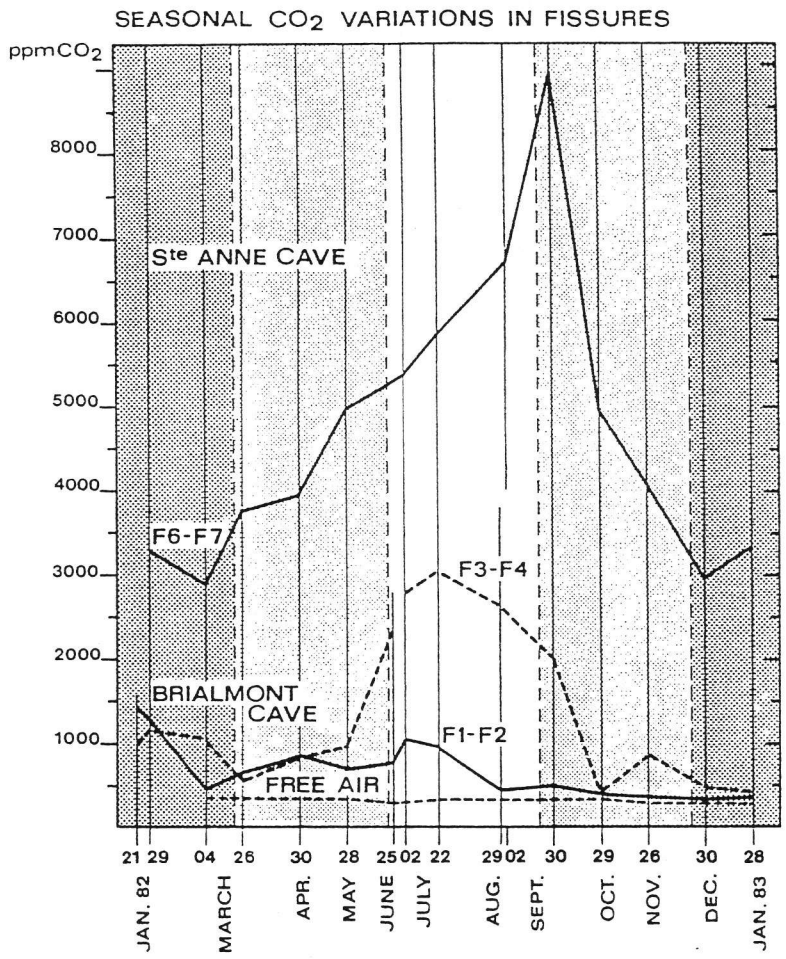

Figure 5. Seasonal evolution of the CO_2 content of the fissures of Ste-Anne and Brialmont Caves. Each line is the mean of the measured values in two adjacent fissures (modified from Gewelt and Ek, 1985)

air) has been found in Ste-Anne cave by Gewelt and Ek (1985). Referring to Figure 10 where 27 measurements carried out on January 7, 1983 along the main passage of Ste-Anne cave are reported, an increase of CO_2 concentration in cave atmosphere from the entrance to the end of the cave can be observed. Linear regression 3 is calculated with all the measures. The correlation coefficient, $r = 0{\cdot}96$ is very high and gives evidence of the existence of a positive linear relation between CO_2 content and distance from the entrance. This phenomenon can first be correlated with the decrease of the ventilation towards the end of the cave. However, it can be seen in Figure 10 that two measurement clusters are distinguishable and that they are separated by a threshold of about 800–1000 ppm. This first group of measurements is located near the entrance and corresponds to the dry part of the cave. The pCO_2 increases from 300 (free air) to 1500 ppm at 160 m from the entrance. The correlation coefficient (linear regression 1) is $r = 0{\cdot}83$. For the second group of measurements (linear regression 2), $r = 0{\cdot}89$ and the CO_2 concentrations are higher towards the sump (end of the cave). It is very interesting to see that the threshold between the two groups of measurements corresponds to the vanishing of the underground river into the lower passage of the cave. The CO_2 content is maximum (3200 ppm) upstream then decreases downstream and, when the underground river disappears in the lower gallery, the CO_2 concentration falls down about 800–1000 ppm and then continues to decrease up to the entrance.

One might assume that the progressive lowering of CO_2 content of the air downstream shows variations of equilibrium between air and water. There is no doubt that the underground river is a purveyor of CO_2 for the

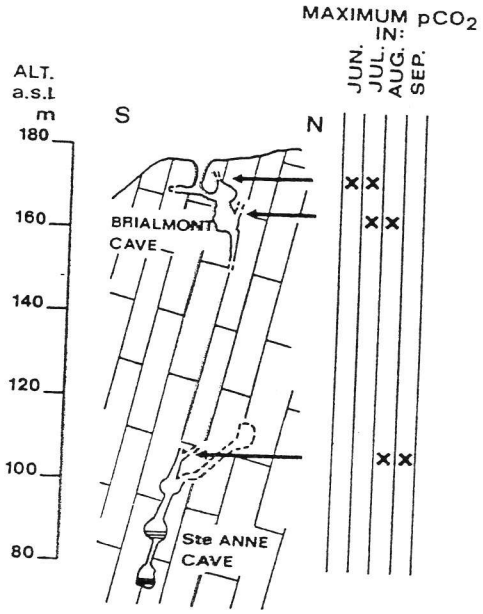

Figure 6. Schematic cross-section of Ste-Anne and Brialmont Caves, at Tilff. Seasonal diffusion of carbon dioxide, as revealed by the measurements summarized in Figures 4 and 5

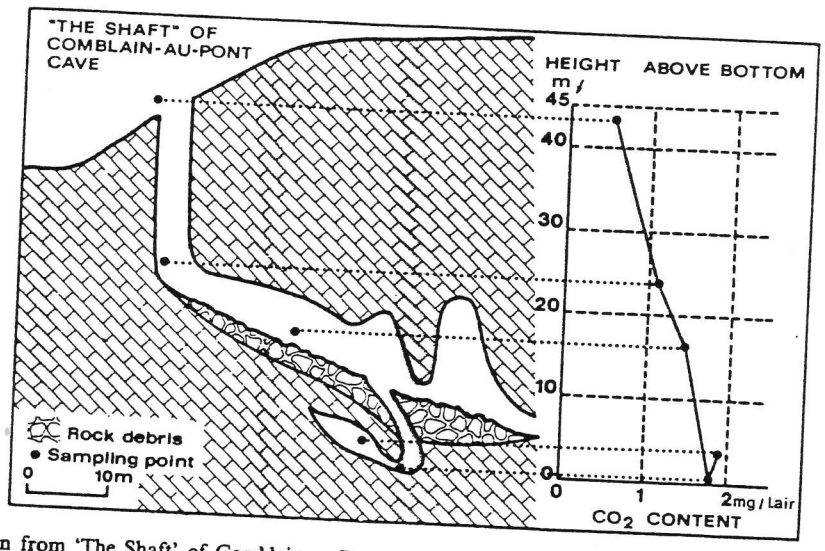

Figure 7. Cross-section from 'The Shaft' of Comblain-au-Pont caye showing CO_2 measurements locations. pCO_2 increases from entrance to bottom (after Delecour *et al.*, 1968)

cave air, in any case when pCO_2 of water is higher than pCO_2 of atmosphere. This CO_2 supply from the water stream seems also to be shown by measurements done 10 cm above the water level: pCO_2 is generally higher just above the water than 160 cm above (see Figure 10).

Contaminations

Some measures we have used for construction of Figures 4 and 5 are too high because CO_2 contamination has been identified. For more details about this feature, we refer to our previous paper (Gewelt and Ek, 1985).

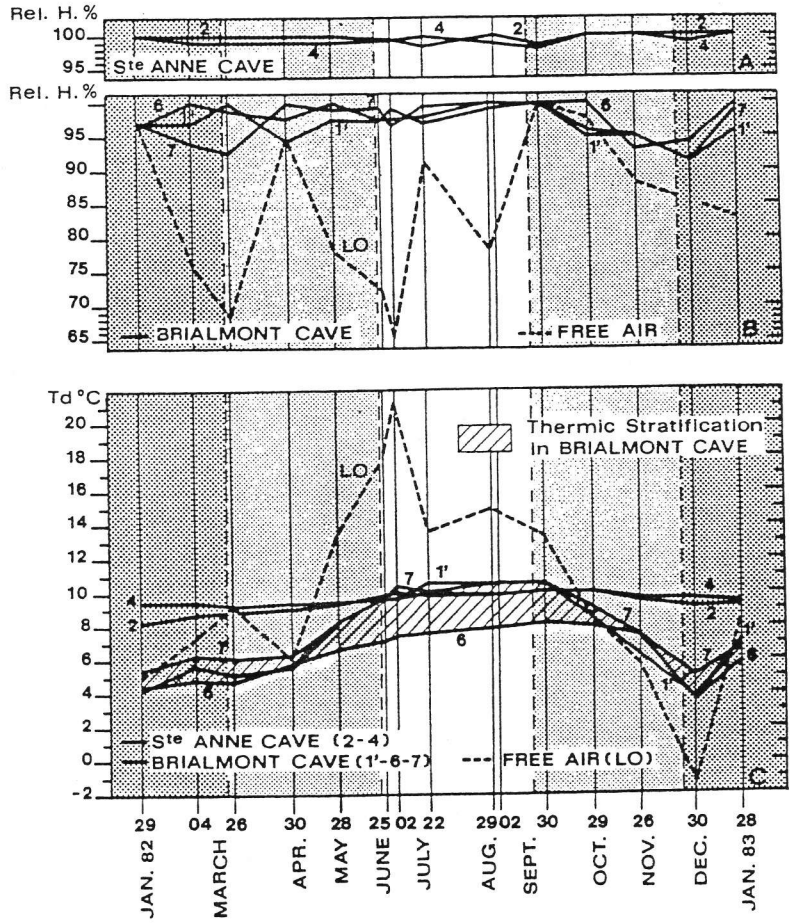

Figure 8. Seasonal evolution of the relative humidity and temperature in Ste-Anne and Brialmont caves. The hachured zone shows the thermal inversion in Brialmont cave (after Gewelt and Ek, 1985)

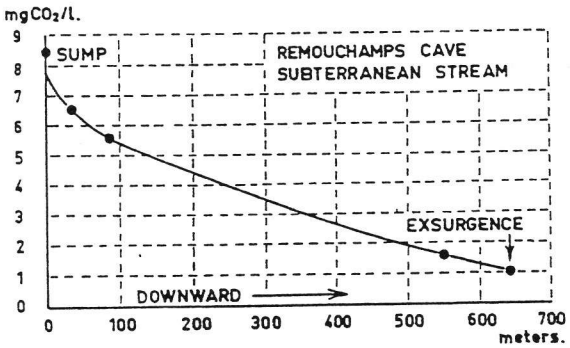

Figure 9. Evolution of CO_2 content of air 20 cm above water level between the sump and the exurgence in the Remouchamps cave. The distance is measured along the stream (after Delecour *et al.*, 1968)

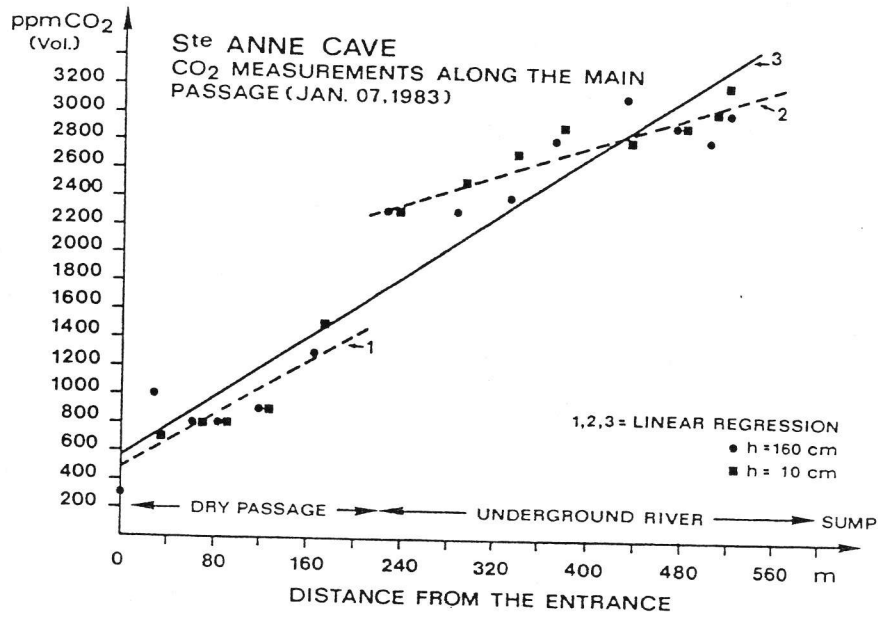

Figure 10. Horizontal evolution of CO_2 content of air in Ste-Anne cave. Linear regressions: (1) $y = 4{\cdot}7 \times + 484{\cdot}7$ ($r = 0{\cdot}83$); (2) $y = 2{\cdot}6 \times + 1719{\cdot}7$ ($r = 0{\cdot}89$); (3) $y = 5{\cdot}3 \times + 563{\cdot}3$ ($r = 0{\cdot}96$) (after Gewelt and Ek, 1985)

We just want to show here some examples of the control of human breathing on CO_2 measurements.

Contamination due to the operator

The following examples will prove the necessity of carrying out CO_2 measurements with a gas absorber system, particularly in confined atmosphere, like fissures and very narrow galleries.

—In Ste-Anne cave (September 26, 1982), a measurement done in a fissure with the CO_2 absorber gives 3800 ppm. In the same fissure, after breathing for five minutes at about 1 m from the measurement site, we measured 5000 ppm. This represents an increase of 32 per cent.

—In Brialmont cave (January 21, 1982) a measurement in the fissure F1 was done rapidly, without gas absorber and avoiding breathing. The result is 1000 ppm. The same measurement was carried out after six exhalations in the fissure and we found 1900 ppm (i.e. increase of 90 per cent).

—In the Trou Joney (Comblain-au-Pont), five measurements were done with and without the CO_2 absorber system. Three pairs of measures have been done in a corridor of about 1 m^2 section: the CO_2 average contents increases by 80 per cent passing from 1·18, 1·66, and 1·72 mg CO_2/l to 2·34, 3·12, and 2·88 mg/l respectively. At the extremity of the cave, in the distal room, CO_2 concentrations pass from 2·03 and 2·32 mg/l to 5·96 and 6·46 mg/l. This represents an increase of 190 per cent (measurements date: December 7, 1969: Ek, unpublished).

Contamination due to the cavers and the tourists

—In Rochefort cave, in a big chamber, the initial CO_2 concentration in the air is 2·30 mg/l. The presence of three operators for five hours gives a measurement of 3·31 mg/l which represents an increase of 44 per cent (measurement date: September 30, 1969: Ek, unpublished).

—In Ste-Anne cave (May 28, 1982), a measure in the gallery gave 4000 ppm; 20 minutes after the passage of 18 cavers (with two carbide lamps), a second measurement was carried out and 4800 ppm was recorded (i.e. an increase of 20 per cent).

—In Remouchamps cave, Mérenne–Schoumaker (1975) has observed, with one of us (Ek), that the presence of about 20 tourists causes an immediate increase of 0·25 mg/l in the narrow galleries. This represents a direct increase of the initial CO_2 content of 6 per cent. During a whole day in the tourist season, the increase is more important: about 30 per cent.

We consider thus that the CO_2 absorber system is a real necessity for measurements in confined places. In another way, the CO_2 production by the cavers is difficult to avoid and we must perhaps deduct a CO_2 background. The CO_2 peaks are also partly correlated with a maximum of caving activity during the summer. Therefore noise reaches a maximum during this period. Another difficulty is that the CO_2 concentration, increased by human CO_2, does not rapidly decrease to its initial value (Ek *et al.*, 1981).

RESULTS AND DISCUSSION FOR CAVES IN OTHER COUNTRIES

Carbon dioxide measurements become increasingly numerous under all climatic conditions. We shall here use the classification of Troll and Paffen (1964) who distinguish, beside the Cool-temperate Zones, two series of colder zones—the Polar and Subpolar Zones and the Cold-temperate Boreal Zone—and two series of warmer zones—the Warm-temperate Subtropical Zones and the Tropical Zone.

The Cold Climatic Zones

In the *Subpolar Zone*, some fifty unpublished analyses by Ek in Labrador (summer 1979), under oceanic subpolar conditions, displayed very low values in soil and in cracks and fissures in dolomite. No true caves were found but, even under a thick soil cover or in deep cracks or just above spring waters, the CO_2 content was always below 600 ppm.

In the *Cold-temperate Boreal Zone*, some 36 measurements carried out in Swedish Lapland, under continental boreal conditions, displayed figures never exceeding 850 ppm in fissures and 450 ppm outside the fissures (Figure 11: Ek, unpublished); 200 ppm were recorded twice close to an underground torrent surface: such a low value, well under the mean value of outside atmosphere, is not unusual in cold climates. The mean of all measurements in 385 ppm ($\pm\sigma = 150$).

Around Lake Mistassini, in the Canadian boreal forest, about 20 analyses (Ek, 1981) displayed values reaching a maximum of 1300 ppm in a small cave. The mean values found were 1100 ppm in the soil, 450 ppm in the open air under forest cover 800 ppm in caves and fissures. It should be noted that all measurements here referred to in cold climatic zones (Labrador, Lapland and Lake Mistassini) were carried out in July and August.

Although much too scarce, these analyses of the air of cold regions show its paucity in CO_2 content. This conclusion is strengthened by the computations of Ford (1971), Woo and Marsh (1977), and Roberge (1979), all based on water analyses in limestone regions, showing that in Canada the cold regions are poor in CO_2 and that the tundra and the alpine meadows are poorer than the boreal forest. Concordant conclusions are

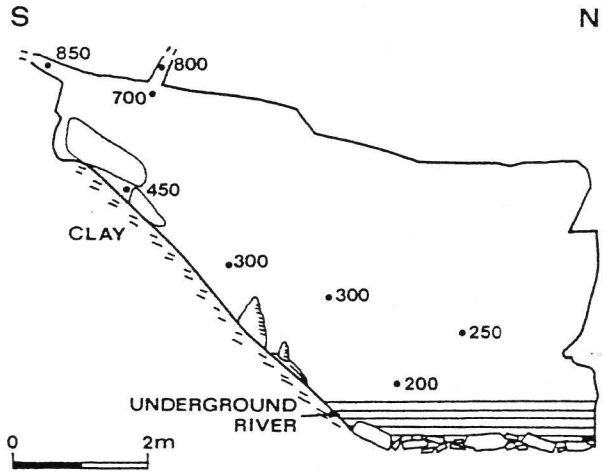

Figure 11. Lower Cave, at Bjorkliden (Swedish Lapland). Cross-section at 16 m from the cave entrance. CO_2 content of the air in ppm (July 26, 1982)

reached by Atkinson *et al.* (1983), by measurements in the air of Castleguard Cave, in the Canadian Rocky Mountains, under the Columbia Icefields.

The Cool-temperate Zones

Under *oceanic and suboceanic climates*, measures are available in England, Belgium, and France.

In England, Atkinson (1975, 1977) observes values rather similar to the ones of Belgium: in GB. Cave, 33 measurements display contents averaging 4100 ppm in galleries and 8200 ppm in the fissures with, in those places, a maximum of 16 000 ppm.

This is concordant with the more than 600 analyses carried out in Belgium, where the range is 300–7000 in the passageways and reaches a maximum of 9000 in fissures (this paper).

In France, where Renault (1982c) lists two to three thousand analyses, the CO_2 content is much varying and is often very high. In the karstic plateaux of the southern border of the Massif Central, the maximum pCO_2 reaches 70 000 ppm. A CO_2 content of 40 000 to 50 000 ppm is frequently reported (Renault, 1982a). Lower ranges are cited in relation with the morphology of caves: caves of medium CO_2 content (10 000 to 30 000 ppm) are generally long horizontal caves; caves of low CO_2 content (1000 to 10 000 ppm) are often horizontal too, but more ventilated, and caves displaying a CO_2 concentration near to the free air (300 to 1000 ppm) are often two-entrance caves, with high air circulation (Renault, 1976).

The CO_2 distribution is related to the cave morphology and the circulation of the air, and its evolution is correlated with meteorological parameters, such as temperature, barometric pressure, and rainfall (see, for example, Renault, 1968, 1976, 1979, 1982a, b, c; Renault and Brunet, 1981). Despite detailed developments on the causes of the high CO_2 contents, one could wish a more critical discussion on possible influences of human presence. As to the techniques and the question of air–water equilibria, see, for instance, Roques, 1956, 1959, 1962, 1963, 1964; Schoeller, 1950.

Under *continental and subcontinental climates*, the measured values show considerable variations as well.

In Quebec, Ek (1981), having carried out some 200 analyses in all seasons, obtains a range of CO_2 content going from 440 to 1100 ppm in the galleries and chambers, whereas the fissures display maximum values in summer (up to 2800 ppm). A closed cave displays higher pCO_2 (Figure 12).

These figures are in accordance with the measurements made in Poland, in the Silesian Upland (Ek *et al.*, 1969), showing, during the snow-melt period of the very early springtime, 500 to 1100 ppm in passageways and a maximum of 1370 ppm in the terminal fissure of the cave.

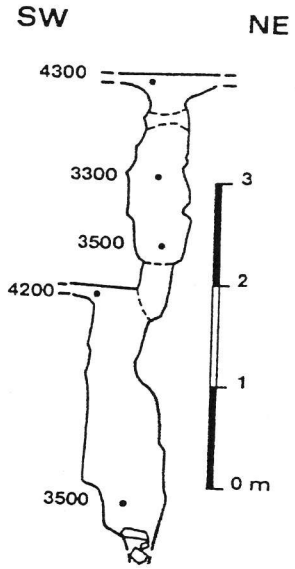

Figure 12. St-Leonard Cave, Montreal (Quebec, Canada). Cross-section nearby the far end of the cave. CO_2 content of the air in ppm (November 22, 1979)

In the caves of Kentucky, 400 to 800 ppm were generally observed by Miotke (1974) in the galleries during the summer; in winter, he noted 400–600 ppm; the maximum value he observed was about 1300 ppm; all these observations were made in rather spacious caves.

In some caves of Ukraine, values ranging from 500 to 40 000 are noted by Klimchuk *et al.* (1981); the highest figures are attributed to the abundance of organic matter in the concerned cave, and the possible (although not measured) occurrence of CH_4, possibly immediately oxydized in CO_2; the occurrence of gypsum is also noted.

Lewis (1981) has studied a cave under a cultivated area, and frequently invaded by organic matter. The author ascribes to the latter fact the high CO_2 content—5000 to 25 000 ppm—of the cave.

Few measurements are known to us in the caves of the *mountain climates of the cool-temperate zones*. In the Swiss Alps, one CO_2 measurement was done by Forel (1865) in a cave near Saint-Maurice. In Bödmerenalp Cave, above the Hölloch Cave, Bögli (1970) finds a very poor CO_2 content (160 ppm), in relation to the high altitude of the cave (1670 m) and the strong wind outside. In the galleries of the Hölloch Cave, CO_2 contents are low—from 250 to 400 ppm—but, in confined places connected with the saturated zone, Bögli (1970) measures 1300 ppm, the highest observed value in this cave. Comparable values were also found during the 1973–1974 winter (Bögli, 1975).

In the Polish Carpathians, Ek *et al.* (1969) have found in four caves, during the snow-melt, 200 to 1100 ppm (40 titrations) and a maximum of 2000 ppm in a fissure.

In the low and middle French Pyrenean Mountains, pCO_2 exceptionally reaches 14 000 ppm (Renault and Brunet, 1981). Generally, however, the CO_2 content of the air is lower in the mountain caves than in caves of lower altitude (Renault, 1968).

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In Northern Italy, a cave of the Ligurian coast displays pCO_2 values ranging from 400 to 800 ppm; the maximum pCO_2 (1500 ppm) was observed in a fissure (24 measurements: Gewelt and Ek, 1983).

In the atmosphere of the caves of Bungonia (New South Wales, Australia), considerable amounts of CO_2, biologically produced, are always present (James, 1977).

In the north of Madagascar, the seasonal evolution of the carbon dioxide of soil air was studied by Rossi (1974). The measured values range from 5000 to 32 000 ppm, this maximum being observed in the humic horizon, at the beginning of the rain season. Measurements carried out above that humic horizon, at the base of the litter, display a lower CO_2 content.

CONCLUSION

It seems clearly established now that the CO_2 present in caves has generally a predominant organic origin. It is thus less abundant, for instance, under cold climates.

Phenomena such as the climatic variations, the seasonal rhythms, the greater abundance in the fissures connecting the caves with the soil, the varied gradients are indeed largely interconnected.

We believe that in some cases, high CO_2 contents are partly resulting from human perturbations. As a consequence, the use of a CO_2 absorber system is necessary, particularly in confined places. In caves frequently visited by cavers or tourists, the human influences on CO_2 measurements are difficult to avoid, but this fact must be taken into account for the interpretation of the results.

Other acids can dissolve limestone in natural environments. But the paramount importance of CO_2 is evident. Limestones, which are so largely biogenic, remain thus after their formation permanently involved in the biological cycles of our planet, of which they form an original and very characteristic component.

Atmosphere and organic reactions are not the only origins of the carbon dioxide; CO_2 can be produced by inorganic reactions, originate from the depth of the Earth, etc. These origins and their relative importance, as well as CO_2 variations during the Quaternary climatic changes are still a wide-open research field. Stable isotopes and ^{14}C analyses could certainly contribute to this topic.

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